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1. Untranslatable words are replaced with asterisks (* **).
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CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1]A manufacturing method of a solid compound which has a porous apatite, wherein pH contacts a calcium content solid compound in 7.0 or more solution, including phosphoric acid ion on a surface at least.

[Claim 2]A manufacturing method of the solid compound according to claim 1 whose phosphoric-acid-ion concentration in solution is 0.1 mol / more than L (liter).

[Claim 3]A manufacturing method of the solid compound according to claim 1 in which 7.0 or more solution adds at least one sort in ammonia, sodium hydroxide, and a potassium hydroxide to solution of orthophosphoric acid, and pH adjusts pH to 7.0 or more including phosphoric acid ion.

[Claim 4]In pH, 7.0 or more solution, including phosphoric acid ion Ammonium dihydrogenphosphate, Diammonium hydrogenphosphate, sodium dihydrogenphosphate, disodium hydrogenphosphate, A manufacturing method of the solid compound according to claim 1 which adds an alkaline substance at least one sort of solution chosen from a group which consists of monobasic potassium phosphate and potassium phosphate, or if needed, and adjusts pH to 7.0 or more.

[Claim 5]A manufacturing method of the solid compound according to claim 1 which is a solid compound in which a calcium content solid compound uses calcium carbonate as the main ingredients.

[Claim 6]A manufacturing method of the solid compound according to claim 5 whose solid compounds which use calcium carbonate as the main ingredients are limestone, a shell, a sea urchin shell, or the coral.

[Claim 7]A manufacturing method of the solid compound according to claim 1 which is a solid compound in which a calcium content solid compound uses calcium silicate as the main ingredients.

[Claim 8]A manufacturing method of the solid compound according to claim 7 which is either of the calcium silicate hydrates which a solid compound which uses calcium silicate as the main ingredients generated by carrying out autoclave curing of the mixture of a wollastonite (wollastonite) and lime, and silicic acid.

[Claim 9]A manufacturing method of the solid compound according to claim 1 whose calcium content solid compounds are a hydrated hardened body of gypsum fibrosum, a hydrated hardened body of Portland cement, or the hydrated hardened bodies of alumina cement.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the solid compound which has a porous apatite on a surface at least. Since an apatite has chemical composition similar to the bone of a vertebrate, or the dental main ingredients and it excels in biocompatibility, are used as a bone, a dental restorative material, etc., but. Especially a porous thing is a material useful as a detoxication decomposition catalyst of organochlorine compounds, such as a biopolymer, living body harmful organicity or the adsorption material of an inorganic ion, medicine gradual release support, support of a microorganism or enzyme, and a trichloroethylene.

[0002]

[Description of the Prior Art]an apatite -- general formula $A_{10}(MO_4)_6X_2$ (here -- A -- 1, such as Cu, Ba, Mg, Sr, Pb, Cd, Zn, nickel, Fe, aluminum, and La, 2, and a trivalent cation.) It is a general term of the mineral in which M has P, As, V, S, Si, etc., and X has composition of F, OH, Cl, O, etc. In this, a living body and the thing with the deepest relation are hydroxyapatite denoted by $Ca_{10}(PO_4)_6(OH)_2$. Hydroxyapatite is general formula $Ca_{10}(PO_4)_6(OH)_{2-x}$ and nH_2O ($0 \leq n \leq 2.5$, $0 \leq x \leq 2.5$), and it is known that calcium and the (OH) radical have unfixed ratio nature.

[0003]The apatite cured body usually sintered hydroxyapatite powder under 900-1100 °C and the hot press conditions of about 10 MPa, and has obtained the cured body of about 100 MPa of compressive strength. As a manufacturing method of a porous apatite, a polymer particle is mixed to the procedure of using the hydraulic reaction of calcium phosphate cement, the apatite particles which carried out grain refining, or it, and fabrication and the procedure of sintering are known. However, by manufacture of the cement powder object, by the latter, by sintering, a high temperature process is needed, respectively, the problem which becomes a cost overrun is pointed out, and development of a simpler and cheap process is demanded at the former.

[0004]

[Problem to be solved by the invention]An object of this invention is to provide the procedure of manufacturing simple, without passing through a high temperature process the solid compound which has at least a porous apatite used as a biopolymer, living body harmful organicity or the adsorption material of an inorganic ion, medicine gradual release support, a microorganism, the support of enzyme, etc. on a surface.

[0005]

[Means for solving problem]As for the manufacturing method of the solid compound which has a porous apatite concerning this invention on a surface at least, pH contacts a calcium content solid compound in 7.0 or more solution, including phosphoric acid ion.

[0006]For example, the hydrated hardened body (gypsum dihydrate) of gypsum fibrosum is converted to an apatite at the following reactions, when diammonium hydrogenphosphate solution is used as solution containing phosphoric acid ion.

$(10-x) \text{CaSO}_4$ and $2\text{H}_2\text{O} + 6.(\text{NH}_4)_2\text{HPO}_4 + n\text{H}_2\text{O} \rightarrow \text{Ca}_{10-x}\text{H}_x(\text{PO}_4)_6(\text{OH})_{2-x}$ and $n\text{H}_2\text{O} + 6(\text{NH}_4)_2\text{SO}_4 + (4-x)\text{H}_2\text{SO}_4 + (18-x)\text{H}_2\text{O}$ -- here, the first chemical formula of the product is a general rational formula of an apatite, and is $0 \leq x \leq 2.5$; $0 \leq x \leq 2.5$.

[0007][as a calcium content solid compound used as a starting material] Natural materials, such as limestone, a wollastonite (wollastonite), a shell, a sea urchin shell, and coral, Or the calcium silicate hydrate which uses as the main ingredients the TOBERUMO light or ZORITO light generated by carrying out autoclave curing of the mixture of lime and silicic acid, They may be any although the aggregate and the reinforcer were further added to artificial raw materials, such as a hydrated hardened body of gypsum fibrosum, a hydrated hardened body of Portland cement, and a hydrated hardened body of alumina cement, or this. As shape of a starting material, arbitrary shape, such as the shape of a powder, the shape of a crush thing, fibrous, tabular, and block like shape, may be sufficient.

[0008]In the generation reaction of an apatite, pH advances in 7.0 or more neutrality or a basic field. It is required to make the pH of reaction mixture high so that pH change may not reach even acidic regions, and to increase the amount of reaction mixture. Especially if the concentration of the phosphoric acid ion in solution is enough to convert a part for calcium in a starting material into an apatite, are not specified, but. It is [more than 0.1 mol / L (liter) / more than 0.5 mol / L / more than 1.0 mol / L] preferably desirable to consider it as the range to 2.5mol/L still more preferably. When pH is less than 7.0 acidity, conversion to a perfect apatite is not obtained, but it carries out subraw [of the stable dibasic calcium phosphate (CaHPO_4 , a mineral name: monetite)] in an acidic range. However, it does not interfere that they are less than pH 7.0 acidic regions in early stages of a reaction. But it is required during a reaction to add alkali and to make pH or more into 7.0 in that case.

[0009]Although reaction temperature in particular is not limited, in order to speed up conversion reaction to an apatite, it is good to consider [not less than 60 °C] it as not less than 80 °C preferably.

[0010]Since reaction time changes with phosphoric-acid-ion concentration, reaction temperature, and porous-apatite-ized thickness of a surface request, it cannot establish a fixed standard, but it is usually a range on several from several hours.

[0011]pH including phosphoric acid ion, [as 7.0 or more solution] What added at least one sort in ammonia, sodium hydroxide, and a potassium hydroxide to solution of orthophosphoric acid, and adjusted pH to 7.0 or more, With or at least one sort of solution chosen from a group which consists of ammonium dihydrogenphosphate, diammonium hydrogenphosphate, sodium dihydrogenphosphate, disodium hydrogenphosphate, monobasic potassium phosphate, and potassium phosphate, What added an alkaline substance if needed and adjusted pH can be used.

[0012]An apatite generated by this invention is a crystal peculiar to a 0.3 micrometer or less in thickness, and 2.0-10 micrometers in width hexagon tabular apatite, and a crevice between the grain child is 0.5 to 0.7 micrometer of porosity.

[0013]Thus, since a solid compound which has the manufactured porous apatite on a surface at least has a pore of several micrometer order, it used various ion exchange ability which support of bacteria, a microorganism, and enzyme and an apatite have, for example, is useful to a purifying agent, a medicine remover, etc.

[0014]When using it for the above uses, it is not necessarily required to porous-apatite-ize to the core part of the calcium content solid compound which is a base, and if a surface (0.3 micrometer - about 20 micrometers) is porous-apatite-ized, it is enough in many cases.

[0015]The conversion reaction from a calcium content solid compound to an apatite is a diffusion or interface reaction rate-limiting type reaction for which apatite-ization advances toward an inside from the outside of a calcium content solid compound. Under the present circumstances, there is a problem of the compatibility of the calcium content solid compound of the problem of generating of the stress distortion in a conversion reaction process and the core part at the time of apatite-izing only a surface and the generated apatite crystal.

[0016]Since a short-time reaction may be comparatively used at low temperature (70-100 °C) like Embodiments 1-4 when apatite-izing only the surface of a particulate matter, it is not necessary to take the problem of generating of stress distortion into consideration. Although compatibility is high and adheres with the porous apatite crystal comparatively firmly in gypsum fibrosum, Portland cement, and calcium silicate (wollastonite), adhesion is weak in limestone. on the other hand, although it was the same calcium carbonate system, by the shell and the compound calcium carbonate system which contains the living thing origins, i.e., protein etc., such as husks and coral, to obtain, since the apatite crystal and hydrogen bond which were

generated on the surface were produced, it joined together firmly, and it turned out that it is stable.

[0017]In the reaction process in the case of on the other hand apatite-izing completely to the deep part of molding bodies, such as tabular [larger] than a particulate matter and block like shape, the stress distortion by the density difference (specific-volume-bulk difference) by the difference in the substance of both layers occurs in the reaction interface of an apatite layer and the calcium content solid compound layer of a core part. When gypsum dihydrate is used as a calcium content solid compound, the density For example, apatite: 3.21g/cm^3 , Gypsum dihydrate: It is 2.32g/cm^3 , hemihydrate gypsum (dehydration of gypsum dihydrate generates above 100°C): 2.7g/cm^3 , and anhydrous gypsum (dehydration of hemihydrate gypsum generates above 120°C): 2.93g/cm^3 . When the interface stress distortion by this density difference is large, or when it generates rapidly, a crack occurs by interfacial peeling. Therefore, it is necessary to set up appropriately reaction mixture concentration, reaction processing time, reaction temperature, and reaction mixture pH, respectively, and to advance conversion reaction. Since a reaction will be accelerated if especially reaction temperature is too high, it becomes easy to produce a crack.

[0018]

[Mode for carrying out the invention]Although an embodiment explains this invention concretely below, this invention is not limited to the following embodiment.

[0019]

[Work example 1]Sodium hydroxide was added to the H_3PO_4 solution of 2 mol / L concentration, and basic phosphoric acid aqueous solution 500mL of pH 11.0 was prepared. After holding the solution to the constant temperature bath set as 70°C and reaching 70°C constant temperature, about 10 g of limestone pulverization things with a particle diameter of $1.0\text{--}1.5\text{ mm}$ were thrown in, and it was made to react for 10 hours. Filtration fractionation was carried out through after-reaction filter paper, and after distilled water washed enough, the limestone which is the particle diameter of $1.0\text{--}1.5\text{ mm}$ which was dried in a 100°C drier for 20 hours, and the surface apatite-ized was obtained. When this thing was observed with the scanning electron microscope, on the limestone surface, the crystal peculiar to a $0.2\text{--}0.3$ micrometer in thickness and $2.0\text{--}3.0$ micrometers in width hexagon tabular apatite was equal to the vertical direction, and was generating. The crevice between crystals was 0.5 to 0.7 micrometer, and was porosity. When the surface was mashed in the agate mortar and having been identified according to the powder X diffraction, it turned out that it is a hydro-oxy apatite. When the powder sample which all mashed the product and pulverized it with the mortar was identified according to the X diffraction, two phases of calcium carbonate and an apatite have been identified. It is limestone with this to an unreacted core part, and it turned out that the

apatite plate crystal is generating the peripheral part to the vertical direction. Reaction time was lengthened further, and when it reacted for 48 hours, agitating with a magnetic stirrer in order to carry out reaction promotion moreover, it became the cloudy milky color slurry form which the apatite particles of the same particle shape distributed mostly.

[0020]

[Work example 2]Ammonia water was added to the H_3PO_4 solution of 1 mol / L, and solution 500mL of PH9.1 was prepared. After holding the solution to the constant temperature bath set as 95 °C and reaching 95 °C constant temperature, about 1 g of 1.0-1.5-mm pulverization things of the shell (ark shell) were put in, and it was made to react for 4 hours. After the reaction, filtration fractionation was carried out through filter paper, and distilled water washed enough. Solid content was dried in a 100 °C drier for 2 hours. The place which contrasted the scanning electron micrograph before the reaction of the shell of an ark shell, and the scanning electron micrograph after a reaction, This reactant also checked that the 0.2-0.3 micrometer in thickness and 4-6 micrometers in width hexagon tabular crystal is closely located in a line with the vertical direction like Embodiment 1, the crevice between crystals was accepted, it had a porous state apatite on a surface, and the particles whose central parts are the shells of an ark shell had been obtained. The plate crystal of the apatite was not accepted in the scanning electron micrograph before the reaction of the shell of an ark shell.

[0021]It has on a surface the porous apatite obtained in Embodiment 2, and the core part carried out sterilization treatment of the 1.0-1.5-mm granular solid compound which is a shell of an ark shell at 140 °C for 2 hours. The Fermentation Research Institute mycoparasite No. (FERMP-12954: the following FERM and abbreviation) 12954 deposited with the Fermentation Research Institute, the Agency of Industrial Science and Technology, at this 0.2 weight % of yeast extract, Large scale culture was carried out so that the shake culture might be carried out at the number of rotations of 130 rpm for 168 hours using the liquid medium which added 0.5 weight % of peptones and adjusted pH to 7.0 and it might become 1×10^9 per medium 1mL. This FERM shows activity to the plant pathogenic microbe of Fusarium by alkalinity by the microorganism which has antimicrobial activity. In order to investigate the microorganism support performance of the sample of Embodiment 2, measuring and agitating 9.95 g as support, FERM of 1mL was diluted with sterile water 1mL, and a total of two mL(s) were added. This thing was supporting FERM of 1×10^8 per 1g of support. The result of having investigated the fixing rate of immediately after incubation under [of 38 °C] temperature conditions, ten days, 20 days, and 30 days after for the purpose of investigating the performance of support is shown in Table 1. Thus, the performance of the obtained support was high. The shell of the ark shell of a starting material did not show support capability at all.

[0022]

[Table 1]

担持体 1 g 当りの菌数 (個)			
直後	1 0 日	2 0 日	3 0 日
1×10^8	1×10^8	1×10^8	8×10^7

[0023]

[Work example 3] A potassium hydroxide was added to H_3PO_4 solution of 1 mol / L concentration, and solution 500mL of PH9.3 was prepared. The solution was held at 100 **, fiber diameter 150-200 micrometers of fiber length of 30-50 micrometers, and 5 g of natural wollastonite (calcium silicate) of the aspect ratios 5-7 were put in, and it was made to react for 10 hours. It dried after filtration washing like an after-reaction embodiment 1, and the quality of a textiles shaped object of porosity which a needlelike apatite crystal which grew in the direction of C axis with the shape of a needle of wollastonite held generated on a surface was obtained.

[0024]

[Work example 4] After adding and kneading water in an ordinary-portland-cement single taste and carrying out granulation to shape with a particle diameter of 2.0-3.0 mm, a granular cement hardened body settled for one week was obtained. Subsequently, ammonia water was added to H_3PO_4 solution of 0.1 mol / L concentration, and solution 500mL of PH9.5 was prepared. The solution was set as 90 **, said about 10 g of granular cement hardened bodies were supplied, and it was made to react for 8 hours. A crevice between grain children by whom an apatite hexagon plate crystal grew up to be a vertical direction obtained mostly about 10 g of porosity granular material which is about 5-10 micrometers on the surface of the same particle diameter after washing dryness like Embodiments 1 and 2 after an end of a reaction.

[0025]

[Work example 5] The gypsum-dihydrate cured body of the one-side shape of about 10-mm cube () [24% of porosity] When it seals to the baroreceptor made of polytetrafluoroethylene resin, and 1.70 g of drying-compression-strength 34MPa abbreviation is held for five days and made to react at 80 ** with about 50 mL(s) of the diammonium hydrogenphosphate solution (PH8.2) of 1.0 mol / L concentration, 54% of porosity, The madreporite without a crack by which the core part of drying-compression-strength 11MPa was constituted from a monetite ($CaHPO_4$), and the outside was constituted from an apatite was obtained. The apatite of this surface part was a porous body which has many crevices among the grain children whom the apatite of the hexagon-like crystal generated to the vertical direction like Embodiments 1, 2, and 4 at the monetite of the core part.

[0026]

[Embodiments 6-16] The result of having changed the concentration, the reaction temperature,

and the reaction time of diammonium hydrogenphosphate solution, and having processed the same gypsum-dihydrate cured body as Embodiment 5 is shown in Table 2 with the result of Embodiment 5.

[0027]

[Table 2]

実施例	(NH ₄) ₂ HP0 ₄ 濃度 mol/L	温度 ℃	時間 日	生成物 表層／芯部	気孔 率 %	圧縮 強度 MPa
5	1.0	80	5	アパタイト／アパタイト	54	11
6	1.0	90	5	アパタイト／アパタイト	55	11
7	1.0	100	5	アパタイト	60	12
8	1.0	120	5	アパタイト	63	11
9	1.0	140	5	アパタイト	62	12
10	1.0	150	5	アパタイト	60	8
11	1.0	140	1	アパタイト／無水石膏	61	15
12	1.0	160	1	アパタイト／無水石膏	62	9
13	1.0	180	1	アパタイト	63	亀裂有り
14	1.0	220	1	アパタイト	65	亀裂有り
15	0.5	100	5	アパタイト／半水石膏	59	4
16	0.5	120	5	アパタイト／無水石膏	61	7

[0028]Embodiments 5-16 are the cases where the gypsum-dihydrate cured body of the one-side shape of about 10-mm cube is porous-apatite-ized. When the concentration of diammonium hydrogenphosphate solution is 1.0mol/L, and reaction temperature is 80 ** and 90 **, even if it applies for five days, a core part does not apatite-ize, but if reaction temperature is not less than 100 **, it will apatite-ize to a core part within five days. If reaction temperature is not less than 180 **, it will apatite-ize to a core part within one day, but a crack is produced. Therefore, in order to obtain a molding body without the crack apatite-ized to the core part, it is desirable to process over many hours at the temperature of not less than 100 ** and 160 ** or less. Thus, it is completely apatite-ized to a core part, and the porous apatite of block like shape which moreover has moderate compressive strength is obtained.

[0029]

[Effect of the Invention]The solid compound which has at least a porous apatite used as a biopolymer, living body harmful organicity or the adsorption material of an inorganic ion, medicine gradual release support, a microorganism, the support of enzyme, etc. on a surface can be manufactured simple, without passing through a high temperature process.

[Translation done.]